

THE EFFECTS OF ACID PASSIVATION, TRICRESYL PHOSPHATE PRE-SOAK, AND UV/OZONE TREATMENT ON THE TRIBOLOGY OF PERFLUOROPOLYETHER-LUBRICATED 440C STAINLESS STEEL COUPLES

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SUMMARY

The boundary-lubrication performance of perfluoropolyether (PFPE) thin films in the presence of passivated 440C stainless steel is presented. The study utilized a standard ball-on-disc tribometer. Stainless steel surfaces were passivated with one of four techniques: (1) submersion in a chromic acid bath for 30 min at 46 °C, (2) submersion in a chromic acid bath for 60 min at 56 °C, (3) submersion in a tricresyl phosphate (TCP) bath for 2 days at 107 °C, or (4) UV/Ozone treated for 15 min. After passivation, each disc had a 400 Å film of PFPE (hexafluoropropene oxide) applied to it reproducibly (± 20 percent) and uniformly (± 15 percent) using a film deposition device. The lifetimes of these films were quantified by measuring the number of sliding wear cycles required to induce an increase in the friction coefficient from an initial value characteristic of the lubricated wear couple to a final, or failure value, characteristic of an unlubricated, unpassivated wear couple. The lubricated lifetime of the 440C couple was not altered as a result of the various passivation techniques. The resulting surface chemistry of each passivation technique was examined using x-ray photoelectron spectroscopy (XPS). It was found that chromic acid passivation altered the Cr to Fe ratio of the surface. TCP passivation resulted in a FePO_4 layer on the surface, while UV/Ozone passivation only removed the carbonaceous contamination layer. None of the passivation techniques were found to dramatically increase the oxide film thickness.

INTRODUCTION

Pretreatment of instrument-bearing components with either a tricresyl phosphate (TCP) presoak (refs. 1 to 10) or a chromic acid passivation bath (refs. 2 and 4), has been performed for over 30 years. Indeed, it has repeatedly been shown that each of these pretreatment procedures improve the bearing's performance in low-speed, boundary lubricated contacts (refs. 1, 2, 9, and 10). Over the years, each of these pretreatments has been incorporated in standard bearing component preconditioning procedures in an attempt to provide additional protection while it is under boundary-lubrication conditions (i.e. during startup and shutdown) (refs. 2 and 8). However, all known reports of improved boundary lubrication performance have utilized either mineral oils or synthetic esters. This is not surprising since the vast majority of TCP and chromic acid passivation qualifying research was performed in the 1960's, when these were the dominant classes of lubricants. These lubricant classes are vastly different than the perfluoropolyether class commonly used today. There has only been one study (ref. 27) that focused on the longevity of a TCP passivated surface lubricated with a PFPE, and none on chromic acid passivated surfaces. Wedeven et al. (ref. 27) concluded that TCP passivation had no effect on the longevity of the lubrication system.

Perfluoropolyethers (PFPE's) have been the preferred liquid lubricants for space applications for over two decades because of their proven tribological performance and other attractive properties (ref. 11) such as low vapor pressure, low chemical reactivity, and wide liquid temperature range. These oils are used in such space mechanisms as actuators, antenna pointing mechanisms, filter wheels, gyroscopes, and scanning mirrors (refs. 12 and 13). However, there have been many incidents during which PFPE-lubricated space mechanisms have shown anomalous behavior (refs. 14 and 15). These anomalies are thought to be the result of PFPE degradation. In order to understand how various passivation techniques might affect the boundary-lubricating performance of PFPEs, it is first necessary to understand how PFPEs degrade.

A number of studies have focused on understanding and modeling the degradation of PFPE lubricants. Research has repeatedly shown that PFPE's degrade while in boundary-lubricated, sliding/rolling contact (refs. 16 to 21) and at elevated temperatures (refs. 22 to 25) losing their desirable properties, including lubricity. Although few models have been proposed to explain the observed degradation, it has been shown that the rate of degradation is dependent upon the surface chemistry of the substrate, and the presence and relative strength of Lewis acids substrates.

Kasai (ref. 22) has shown that the thermal catalytic degradation of a PFPE is dependent upon the strength of the Lewis acid present and has proposed a chemical degradation mechanism for PFPE's. He postulated a mechanism in which Lewis acids act as a catalyst that promotes an intramolecular disproportionation reaction which results in polymer-chain degradation.

Other static degradation studies, conducted to look at the effects of certain metals or metal alloys in the presence of particular PFPE's, have shown that PFPE degradation is highly dependent upon the chemistry of the substrate. For example, an unbranched PFPE lubricant showed more degradation at 288 °C in the presence of M-50 steel and Ti-4Al-4Mn than in contact with either pure titanium or pure aluminum (ref. 24).

Some studies have applied the concept of modifying one, or both of the surface chemistries by coating or ion implanting the surface(s), and observing the associated tribological characteristics. Carré (ref. 19) demonstrated that the PFPE boundary-lubricated wear life was increased by a factor of 5 to 10 by using TiN-coated 440C test specimens. TiC-coated 440C and Si₃N₄ ceramic ball bearings have also been shown to have greater longevity compared to their 440C counterparts when PFPE lubricated (refs. 18 to 20). In Carré's studies (refs. 19 and 20) it was concluded that the hard coatings and ceramic material prevented the formation of Lewis acids, thus halting the Lewis acid-induced degradation of the PFPE. Shogrin et al. (ref. 26) demonstrated that implanting 440C substrates with either Ti with a carbon (CH₄) back pressure, or Ti without a carbon back pressure enhanced the lubricating lifetimes of the PFPE. It was concluded that the resulting microstructures inhibited the formation of reactive sites.

Yet another way to inhibit tribo-induced degradation of the lubricating PFPE may be to passivate the contacting surfaces. The passivated surfaces might inhibit the formation of Lewis acids in the presence of fluorinated oils, or decrease the relative availability of reactive sites on the surface, thus, extending the lubricated lifetime of the couple.

The objective of this work was to study the effect of various passivation techniques on the lubricating-lifetime of a PFPE-lubricated 440C stainless steel couple in sliding contact. The two passivation techniques mentioned, chromic acid passivation (similar to 2 and 4) and TCP (similar to 1 to 10), as well as a modified chromic acid passivation technique (which uses a higher temperature and a longer reaction time), and UV/Ozone treatment (ref. 30) will be studied. UV/Ozone treatment has been used to remove carbonaceous contamination from surfaces. A demonstration of their effectiveness in prolonging lubricity is sought rather than a detailed description of the associated chemical degradation mechanism(s).

EXPERIMENTAL

Materials

Discs and bearing balls made from 440C stainless steel (fully hardened) were used. The 440C discs were 17.5 mm (11/16 in.) in diameter and 4.76 mm (3/16 in.) thick. Each disc was polished to a mirror finish having an arithmetic roughness average, R_a, of ~ 0.01 μm. The bearing balls were Grade 10 and had a diameter of 9.53 ± 0.00102 mm (3/8 in. ± 0.00004 in.).

A variety of surface preparations were tested. A portion of the disc/ball pairs were tested unlubricated and untreated (unpassivated), while others were tested unlubricated after being treated (passivated). Still others (passivated and unpassivated) were tested after lubricating the disc. None of the bearing balls were lubricated prior to testing. Throughout this report the term "unpassivated" is used rather loosely. When used, it refers to pairs that have not been passivated or UV/Ozone treated. The lubricant used was a commercial

perfluoropolyether (PFPE), based on hexafluoropropene oxide (HFPO). Typical properties of this PFPE are given in Table I.

Specimen Preparation

All disc/ball pairs were ultrasonically cleaned in hexane, acetone, and finally methanol for approximately ten minutes each. The pairs were then blown dry with nitrogen and promptly covered to minimize dust contamination. Disc/ball pairs that were not passivated and did not have PFPE applied to the disc were placed in a N₂ atmosphere (R.H. < 2 percent) at ambient temperature where they remained until tribo-tested. Unpassivated discs that had PFPE applied, were lubricated and then placed in a N₂ atmosphere, with their accompanying unpassivated ball. Disc/ball pairs that were treated were done so using one of the four following procedures.

Chromic-Acid Passivation.—Clean disc/ball pairs were passivated in one of two ways using a solution consisting of 2.0 gm sodium dichromate (Na₂Cr₂O₇·2H₂O), 20 ml concentrated nitric acid (HNO₃), and 80 ml deionized H₂O. Specimens were immersed in the solution either for 30 min ± 10 sec while heated to 46 ± 0.1 °C, or for 60 min ± 10 sec while heated to 56 ± 0.1 °C. The samples were then removed and thoroughly rinsed using two successive deionized H₂O baths. Samples were then blown dry with nitrogen and promptly covered.

Tricresyl Phosphate (TCP) Passivation.—Disc/ball pairs were immersed for 48 hr ± 5 min in neat tricresyl phosphate (TCP) heated to 107 ± 0.1 °C. (The TCP was purchased in accordance with the requirements of TT-T-656b). The samples were then ultrasonically cleaned in hexane, acetone, and methanol for approximately 10 min each. Samples were then blown dry with nitrogen and promptly covered.

UV/Ozone Treatment.—Disc/ball pairs were UV/ozone treated for 15 min to remove carbonaceous contamination (ref. 30) which begins to reform immediately after this treatment.

Treated discs that did not have PFPE applied to them, and all treated bearing balls were placed in a dry N₂ atmosphere where they remained until tribo-tested. Treated discs that had PFPE applied to them were lubricated (UV/ozone treated discs were lubricated within 5 min of treatment) and then placed in the same dry N₂ environment.

XPS Analysis of Passivated Surfaces.—A disc passivated by each of the four techniques and a baseline disc (untreated) were analyzed using x-ray photoelectron spectroscopy (XPS). The XPS analysis was done in a Vacuum Generator (VG) ESCALAB MkII system equipped with a Mg K_α x-rays source. XPS analyzes the top several atomic layers of the sample providing both elemental and chemical state information. An area of 2×5 mm² was analyzed on each of the respective surfaces. Survey spectra, from 0 to 1200 eV Binding Energy, were taken to determine which elements were present followed by high resolution energy windows for each of the major elements detected on the surface to determine their chemical state. There is typically a 5 to 10 percent error associated with the resulting calculated atomic concentrations.

Application of Lubricant Films by Deposition from a Solution

Thin film deposition was accomplished by using the apparatus shown in figure 1. This is a derivative of the deposition process known as dipping. In this process, a specimen is lubricated by slowly withdrawing it at a constant speed from a solution of the fluid in a volatile solvent. As the solvent evaporates, a thin film of the nonvolatile fluid remains on the surface. In this procedure, both solution concentration and withdrawal speed govern the applied film thickness (ref. 31). For the apparatus used in this study, gravity driven solution flowed past the stationary specimen. The surface speed that the solution attained as it flowed past the specimen was approximately 0.8 mm/sec. Each lubricated disc was done so using a concentrations of 5.0 g of PFPE lubricant in 100 ml of solvent (a perfluorinated cyclobutane).

Lubricant Film Thickness Measurements

The PFPE thickness on each disc was measured using an infrared microscope (μ-FTIR) in the reflectance mode using a Grazing Angle Objective (GAO) with a Mercury Cadmium Telluride (MCT) detector. The instrument's spectral resolution was 4 cm⁻¹. A gold coated glass slide was used as the background. Absorbance as a function of wave number was determined for each film at three different radii on the disc's surface, approximately 120° apart using an analysis spot diameter of 100 μm.

Theoretical thin film optical calculations have been performed to model the PFPE film's behavior in the infrared spectral region (ref. 32). These results are plotted as absorbance of the 1313 cm^{-1} band as a function of film thickness, and shown in figure 2. After experimentally obtaining the absorbance of the 1313 cm^{-1} band, the corresponding film thickness was obtained using figure 2.

The FDD apparatus produced PFPE film thicknesses of $\sim 400 \text{ \AA}$. Lubricant uniformity across any one surface was ± 15 percent. The error associated with surface-to-surface film thickness repeatability was ± 20 percent.

Tribological Testing

Tribological testing of each disc/ball couple was performed on the fixed-ball-on-disc tribometer shown in figure 3. All tests were performed using a relative sliding speed of 0.05 m/s and a 3-N normal load which generated an initial Hertzian contact pressure of $\sim 0.69 \text{ GPa}$. All tests were run in dry N_2 (< 2 percent RH) at ambient temperature ($\sim 25 \text{ }^\circ\text{C}$). The friction force as a function of disc revolutions (cycles) was recorded for each test (one wear track).

After a test, the ball support fixture and ball were rotated to expose an unworn surface on the ball and the fixture was extended so the ball would contact the disc at a different radius. By doing this, three wear tracks, 1.59 mm (1/16 in.) apart, could be worn on each disc.

RESULTS AND DISCUSSION

Establishment of the Lubricant-Failure Criterion

Lubricant failure occurred when the friction coefficient increased from an initial low value to a value typical of an unlubricated, unpassivated disc/ball couple. When this failure occurred, it was argued that the protective layer(s) (applied lubricant, surface oxide, and/or additional passivation layer) either wore off, ruptured or broke down. Figure 4 shows the mean friction coefficient as a function of cycle number for three wear tracks on two separate unlubricated, unpassivated couples. Mean friction coefficient was the mean of the friction coefficients of the complete revolution over the indicated cycle. Typically, friction-coefficient fluctuations over a cycle were ± 0.06 (maximum: ± 0.15) about the mean. The mean friction coefficient data all lied between 0.63 and 0.8. Thus, an increase in mean friction coefficient above 0.63 was indicative of failure and was defined as the failure limit. The number of rotational cycles that can be applied to the lubricant film on a wear track before the friction rose above the failure limit was the film's lubricating lifetime.

It was also important to know if the passivation process itself changed the failure limit, therefore, one disc passivated at each condition was tested unlubricated. Initially, the chromic-acid and TCP passivation samples exhibited lower mean friction coefficients (0.26 to 0.3), but then rose near-linearly above the failure limit at different rates. The value of the TCP passivated surface continued to rise to ~ 0.8 , where it then dropped to a value of ~ 0.53 in the course of one cycle, after which it again rose to failure and stayed. The UV/Ozone treated surfaces showed no improvements and behaved the same as the untreated samples depicted in figure 4. Table II summarizes these data. The UV/Ozone treated results are not shown because no improvements were observed with this technique. In this table, the average values appear outside the parentheses, whereas the ranges are contained within the parentheses. These data suggest that both chromic-acid passivation techniques improved the friction coefficient for a brief time, whereas TCP passivation extended the low friction coefficient for an extended time.

Lubricated Results

Lubricated, unpassivated discs/ball couples were tested. A typical plot of mean friction coefficient vs. cycle number is shown in figure 5. These particular data were taken from a disc with a $\sim 70 \text{ \AA}$ HFPO film. The mean friction coefficient begins to rise from ≤ 0.3 near 200 cycles and crosses the failure line of 0.63 at ~ 370 cycles (lubricant lifetime = 370 cycles).

This general trend was typical for the samples used in this study. In these tests the maximum variation of the friction coefficient before it began to rise (here at ~ 200 cycles) was ± 0.02 . This relatively small variation indicated that the entire wear track was uniformly experiencing the benefits of full boundary lubrication from the PFPE. After the initial rise, the variation of friction coefficient grew as the number of cycles increased until, at the failure limit, it typically had a variation of ± 0.1 (maximum: ± 0.20 , minimum: ± 0.03).

As a test progressed, different locations on the wear track lost their lubricity at varying rates, which accounted for the spread in friction coefficient values seen over one cycle (indicated by the variation noted

above). Although the rate of lubricity loss over the entire wear track varied, and the variation increased as the number of cycles increased, the mean friction coefficient continued to rise, signifying an overall loss of lubricity.

Beyond failure, variations of the friction coefficient over a rotational cycle, as well as the mean friction coefficient were sporadic. On some wear tracks, the mean friction coefficient dipped below the failure line after it had reached failure (rarely dipping below ~0.4). This decrease was caused by the rapid growth of the wear scar's width coming into contact with fresh, unused PFPE lubricant. This fresh lubricant decreased the friction coefficient before it too degraded, causing the mean friction coefficient to again rise past the failure limit. These sporadic variations were also considered an indicator of failure.

After performing a number of the tests, it was apparent that the lifetimes had a significant spread in their values for each of the unpassivated and passivated conditions. These spreads in lifetime appeared random, as they were not dependant upon either a particular disc or radius of wear track. Weibull statistics (ref. 33) were used to characterize these data.

The Weibull plot for the unpassivated disc/ball couples PFPE-lubricated is shown in figure 6. Each data point represents the lubricated lifetime of one wear track. The Median Rank Line represents the most probable failure history for the samples, that is, the fraction of a group of samples that can be expected to fail (i.e., exceed 0.63 friction coefficient) as a function of the number of sliding cycles. This line suggests 60 percent of a given number of tests can be expected to undergo failure at or before ~3700 cycles. Given an infinite number of tests, the 90 percent confidence bands were in the region in which the lifetimes of 90 percent of those tests would reside.

The usefulness of a Weibull plot can be demonstrated by relating it to the reliability of a component. For a typical space bearing, which cannot generally be retrieved for maintenance, reliability is very important. If > 99 percent reliability is desired in a lubricated couple, then the number of cycles that it is allowed to experience should be less than the value that will generally produce failure 1 percent of the time. For the unpassivated samples in figure 6, 1 percent of them are predicted to fail by ~120th cycles. By comparing each passivation technique's Weibull plot to the plot of the unpassivated specimens (fig. 6), and to each other, produces their relative performance. Their relative performance is summarized after the next section.

Passivated-Lubricated Results

The Weibull lifetime distributions of the four passivation techniques and the unpassivated technique (from fig. 6) are shown in figure 7. This figure indicates that the predicted lifetimes are all very similar. The 90 percent confidence bands of the five plots (not shown) all overlap over most of the range of each Median Rank Line. Therefore, within 90 percent assurance, it is predicted that no one passivation technique out perform another. These plots indicate that none of the passivation techniques neither exhibited superior nor grossly sub-standard performances relative to the unpassivated surfaces.

The 1 and 60 percent predicted lifetimes are tabulated in Table III. Again, statistically one cannot say that any one technique out performed another. The possible exception to that may be the 1 percent failure lifetimes. TCP passivated samples have a 1 percent failure of ~1000 cycles, which is nearly an order of magnitude higher than that of the unpassivated result of ~120 cycles. This difference is caused by the greater slope (more reproducible data) of the TCP passivated samples. More tests would have to be run to verify this possible distinction.

Given the sliding nature of these tests and the thinness of both the lubricant and the passivation layers, one might have predicted this result. However, the unlubricated tests did show measurable differences between the various techniques. In addition, this same procedure was used to evaluate differences in various ion implanted surfaces (ref. 26). The thicknesses of the implanted layers were on the same order as the thicknesses of the passivated layers. Finally, it has been known for decades that the TCP presoak and the low temperature chromic acid passivation techniques provide additional protection in boundary lubricated contact while lubricated with either mineral oils or esters (refs. 1 to 10). Thus, the authors conclude that none of the passivation techniques tested increased the longevity of the perfluoropolyether-lubricated wear couples.

XPS Analysis of the Passivated Surfaces

By using XPS oxide-to-metal peak area ratios, it was estimated that the oxide film thickness for all the surfaces (Cr_xO_y , Fe_xO_y or FePO_4) was less than ~50 Å. A summary of the atomic percent of selective elements obtained from the XPS analysis of a surface passivated using each of the four techniques and the

unpassivated surface is shown in Table IV. The unpassivated surface had Cr to Fe ratio of 0.34, and a distinct carbonaceous contaminating layer as indicated by the C atomic percent.

The low temperature chromic-acid passivated sample had a high Cr/Fe ratio (2.3). This indicates that the passivation solution selectively attacked and dissolved the near-surface iron oxide, while leaving the more inert chromium oxide intact. This would account for the change in Cr to Fe ratio in the first few atomic layers of the surface. The higher nitrogen atomic percent on this surface was caused by the presence of nitric acid.

The surface of the sample passivated with the higher temperature chromic-acid solution has a lower Cr to Fe ratio than the lower temperature chromic-acid passivated surface, but a higher ratio than the unpassivated surface. The difference in the Cr to Fe ratios for the two passivation techniques is considered to be within the random error associated with the passivation procedure. It is noted that the two passivation techniques resulted in very similar surface chemistries, which indicates that increasing the passivation time and temperature was relatively ineffective. The fact that the Cr to Fe ratio is higher than the unpassivated surface indicates that the Fe atoms are being selectively removed at a higher rate than the Cr atoms.

Evidence for iron phosphate formation from TCP passivation is shown in figure 8. The figure compares the XPS spectra of the Cr region of the high-temperature chromic-acid passivated surface to that of the TCP passivated surface. The chromic-acid passivated surface has a large $\text{Cr}^{\delta+}:\text{Cr}^{\circ}$ metal peak, whereas, the TCP passivated spectra contains a much smaller $\text{Cr}^{\delta+}:\text{Cr}^{\circ}$ metal peak. This, along with the presence of the 12 atomic percent P, and the decreased Cr to Fe ratio are consistent with the formation of an iron phosphate surface layer.

As evidenced by a decrease in carbon on the UV/ozone treated surfaces, UV/ozone treatment preferentially removes the carbonaceous contamination layer. UV/ozone treatment was not found to increase the oxide film thickness of these samples. This fact has been previously documented (ref. 30).

SUMMARY OF RESULTS

1. None of the passivation techniques significantly increased the oxide film thickness.
2. Using x-ray photoelectron spectroscopy, it was found that chromic acid passivation increased the Cr to Fe ratio of the surface. Couples passivated with chromic acid, tested unlubricated, experienced an improvement in friction coefficient for a short time. However, chromic acid passivation did not affect the PFPE lubricating lifetime.
3. TCP passivation resulted in a few-monolayer-thick FePO_4 layer on the surface. TCP passivated couples tested unlubricated experienced improved, low friction for a short duration. However, an improvement in PFPE-lubricating lifetime was not observed after TCP passivation.
4. UV/Ozone treatment removed the carbonaceous contamination layer on the surface but did not alter either the unlubricated or the PFPE-lubricated lifetimes.
5. The PFPE lubricated lifetime of 440C couples did not definitively change as a result of the various passivation techniques.

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TABLE I. —SELECTED PROPERTIES OF THE PFPE USED IN THE STUDY

Average Molecular Weight	11000 amu
Vapor Pressure at 20°C at 50°C at 100°C	3×10 ⁻¹⁴ Torr 2×10 ⁻¹² Torr 1×10 ⁻⁹ Torr
Kinematic Viscosity at 20°C at 50°C at 100°C	2717 mm ² /s (centistoke) 444 mm ² /s 63 mm ² /s
Density at 20°C at 50°C at 100°C	1.92 g/cm ³ 1.87 g/cm ³ 1.78 g/cm ³
Surface Tension at 25°C	19 dynes/cm

Table II.—UNLUBRICATED WEAR TEST RESULTS

Surface passivation treatment	Initial mean friction coefficient	Number of cycles until failure	Tracks tested
Chromic-acid, low temperature	0.27 (0.24-0.27)	5 (4 to 6)	5
Chromic-acid, high temperature	0.26 (0.24-0.27)	9 (7 to 10)	4
Tricresyl phosphate	0.29 (0.27-0.34)	68 (60 to 85)	5

TABLE III—SUMMARY OF DATA OBTAINED FROM WEIBULL PLOTS

Surface passivation/treatment	1 percent failure	60 percent failure
Unpassivated	120	3700
Chromic-acid, low temperature	440	3600
Chromic-acid, high temperature	440	7000
Tricresyl phosphate	1000	2300
UV/Ozone treatment	240	5000

TABLE IV.—ELEMENTAL SURFACE CONCENTRATION FOR EACH PASSIVATION TREATMENT OBTAINED BY XPS

Atom percent	C	O	Fe	Cr	Cr/Fe Ratio	Miscellaneous
Unpassivated	28	54	13	4.4	0.34	0.5 N
Chromic-acid, low temperature	23	61	4.3	10	2.3	0.9 N
Chromic-acid, high temperature	19	61	10.1	9.3	0.93	0.9 N
Tricresyl phosphate	24	58	4.6	1.1	0.24	0.8 Na 3.5 Ca 12 P
UV/Ozone treatment	18	58	18	6	0.33	<0.1 N

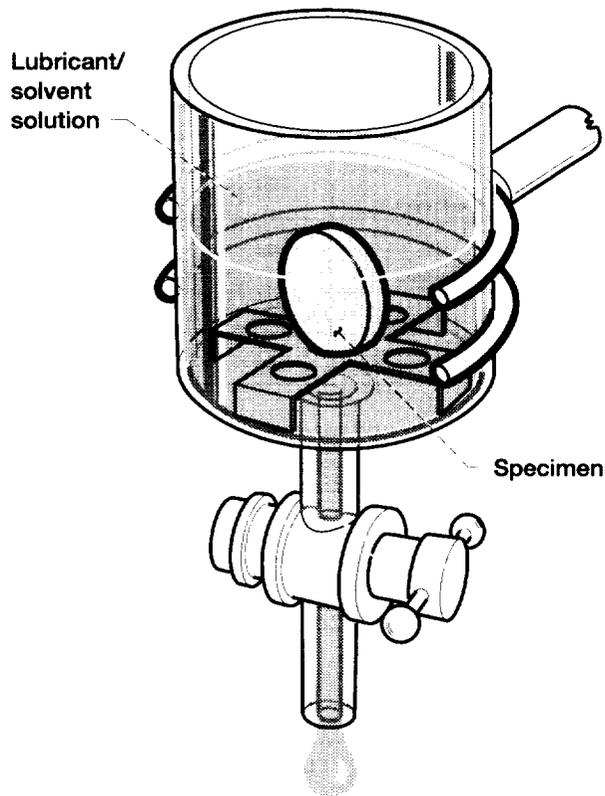


Figure 1.—Film deposition device (FDD).

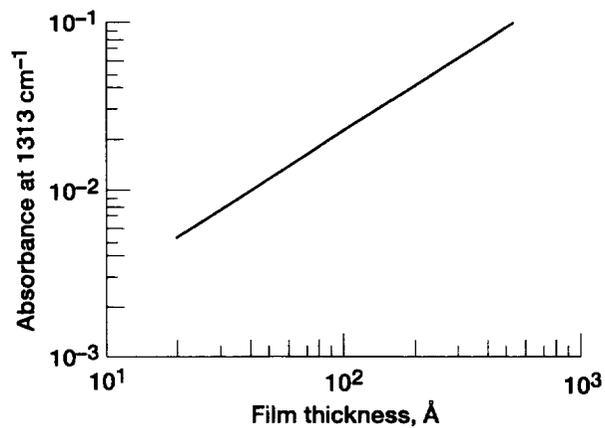


Figure 2.—Calculated IR absorbances for the 1313 cm⁻¹ band of HFPO as a function of film thickness.

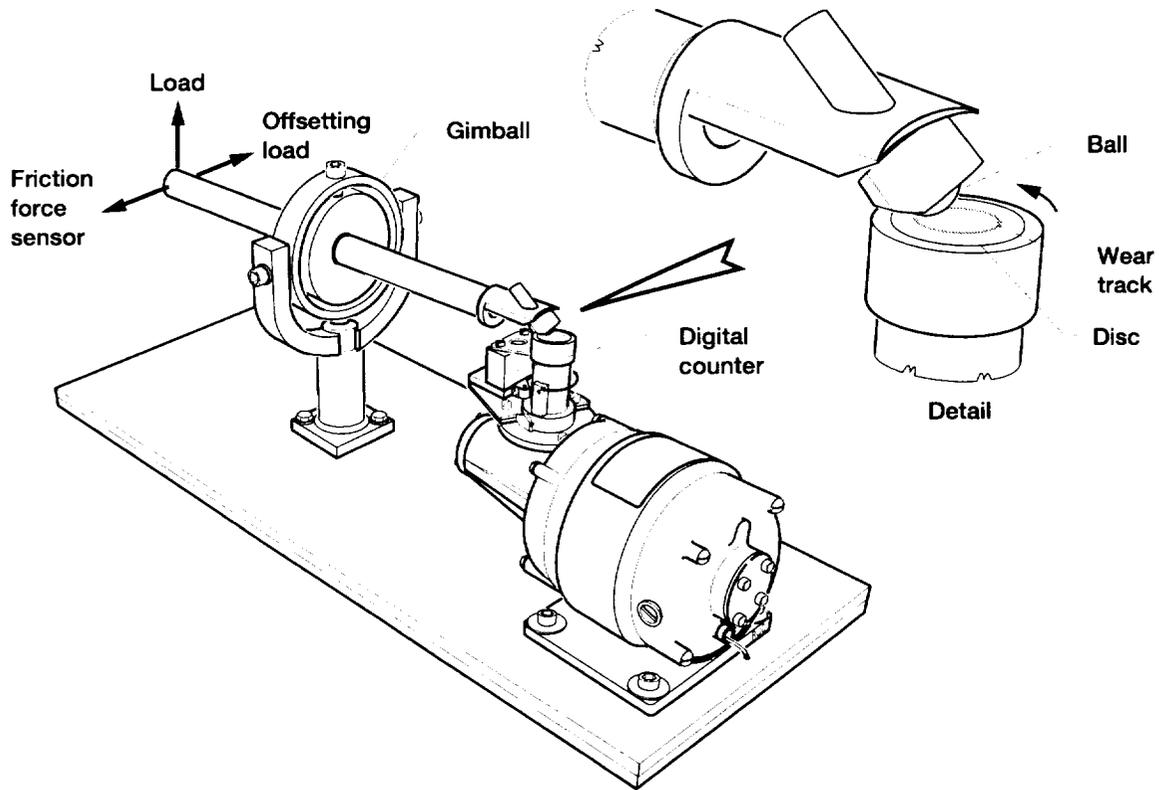


Figure 3.—Ball-on-disc tribometer.

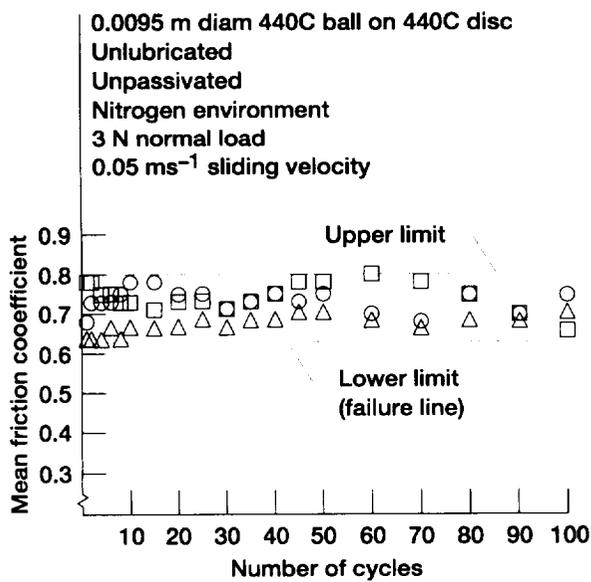


Figure 4.—Typical friction coefficient data for unpassivated, unlubricated disc/ball couples (ref. 26).

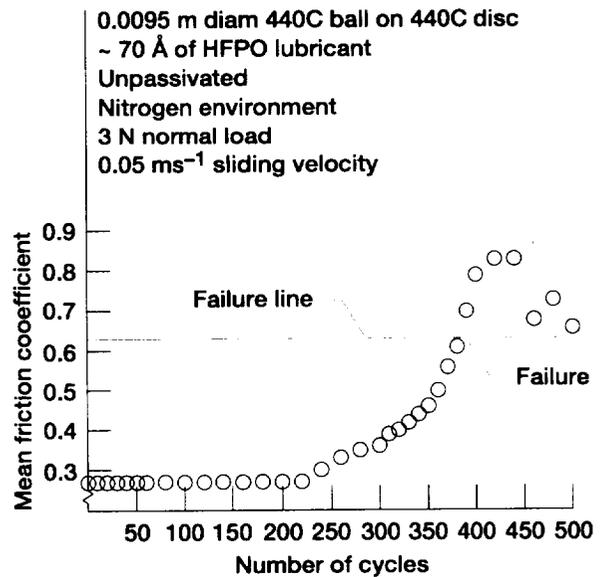


Figure 5.—Typical friction coefficient data for unpassivated, lubricated disc/ball couples (ref. 26).

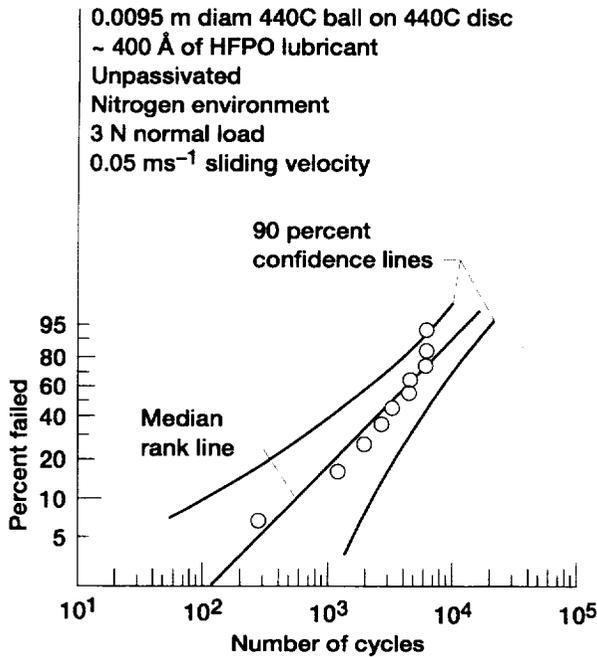


Figure 6.—Weibull distribution lifetimes for unpassivated, lubricated disc/ball couples.

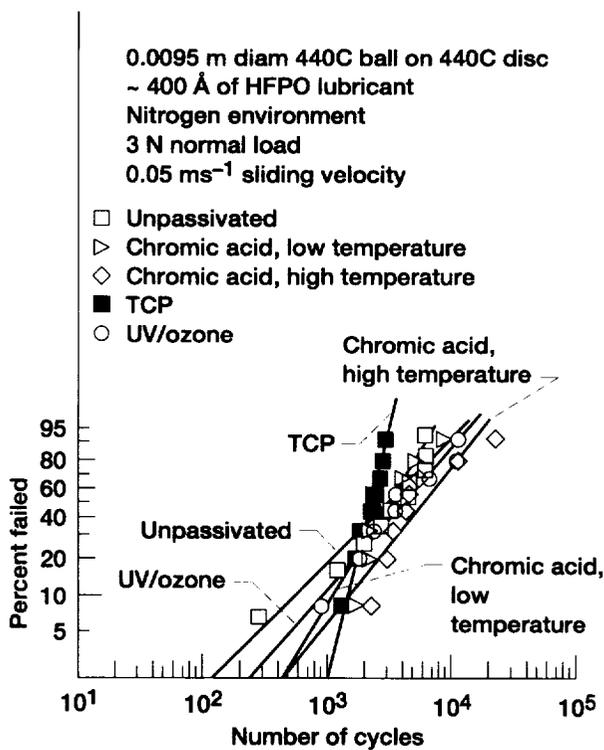


Figure 7.—Effect of passivation on Weibull distribution lifetimes for lubricated disc/ball couples.

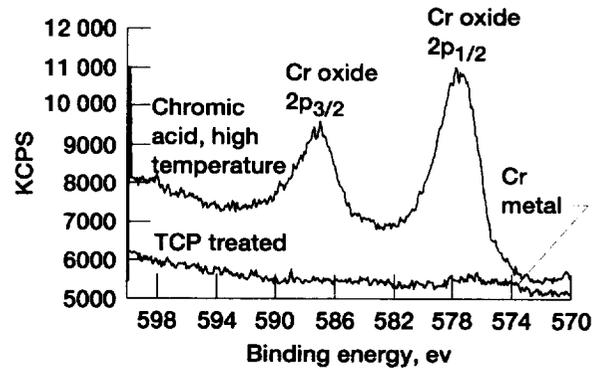


Figure 8.—XPS spectra showing the chromium oxide region of both the high temperature chromic-acid, and TCP passivated surfaces.

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13. ABSTRACT (Maximum 200 words) The boundary-lubrication performance of perfluoropolyether (PFPE) thin films in the presence of passivated 440C stainless steel is presented. The study utilized a standard ball-on-disc tribometer. Stainless steel surfaces were passivated with one of four techniques: 1) submersion in a chromic acid bath for 30 minutes at 46 °C, 2) submersion in a chromic acid bath for 60 minutes at 56 °C, 3) submersion in a tricresyl phosphate (TCP) bath for 2 days at 107 °C, or 4) UV/Ozone treated for 15 minutes. After passivation, each disc had a 400 Å film of PFPE (hexafluoropropene oxide) applied to it reproducibly ($\pm 20\%$) and uniformly ($\pm 15\%$) using a film deposition device. The lifetimes of these films were quantified by measuring the number of sliding wear cycles required to induce an increase in the friction coefficient from an initial value characteristic of the lubricated wear couple to a final, or failure value, characteristic of an unlubricated, unpassivated wear couple. The lubricated lifetime of the 440C couple was not altered as a result of the various passivation techniques. The resulting surface chemistry of each passivation technique was examined using X-ray photoelectron spectroscopy (XPS). It was found that chromic acid passivation altered the Cr to Fe ratio of the surface. TCP passivation resulted in a FePO ₄ layer on the surface, while UV/Ozone passivation only removed the carbonaceous contamination layer. None of the passivation techniques were found to dramatically increase the oxide film thickness.				
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